Characterization of cationic dextrin prepared by ultra high pressure (UHP)-assisted cationization reaction[☆]

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ABSTRACT

Cationic dextrins were prepared through substitution reaction of dextrin with low and high addition levels of 2,3-epoxypropyltrimethylammonium chloride (ETMAC), respectively. Conventional cationization reactions were carried out for 5 h under continued stirring. UHP-assisted cationization reactions were conducted at three pressurization levels of 100, 300 and 500 MPa for a pressure holding time of 30 min. Degree of substitution (DS) of UHP-assisted cationic dextrins ranged from 0.58 to 1.51, and in general, their DS values were enhanced with increasing pressure levels. FT-IR and ^{13}C NMR spectra indicated the presence of C—N bond, which provided clear evidence about incorporation of cationic moieties onto dextrin molecules. In flocculation test, UHP-assisted cationic dextrin revealed higher flocculating activity. Overall results suggested that UHP-assisted cationization reaction could modulate reactivity and flocculating activity of dextrin by controlling pressure levels and reaction mixture compositions, and cationic dextrins likely possessed a higher potential to replace synthetic polymer-based flocculants.

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1. Introduction

Wastewater recycling system, long-established and widely used in industries, involves the solid–liquid separation through flocculation of dispersed solids in wastewater by addition of coagulants and flocculants (Ruehrvein & Ward, 1952; Smellie & La Mer, 1958). For wastewater treatment, synthetic, polymeric flocculants such as poly(acrylamide) and poly(acrylic acid) are generally utilized, due to their low cost and easy use. Nevertheless, safety and environmental concerns may arise from utilization of commercial synthetic flocculants that may possess the toxic monomers and chemical residues from incomplete synthesis and chemical additives, and the non-biodegradability. Also, there appears to be the worldwide lacks of oil resources which are the first raw material for the polymer synthesis. Thus, there have been recent attempts to replace synthetic polymers into natural and processed carbohydrate-based polymers (i.e., starch, cellulose, chitosan, dextrin, and non-starch polysaccharide) as sources for preparing flocculants (Wei, Cheng, & Zheng, 2008). While natural carbohydrate-based polymers are renewable, biodegradable, and non-toxic (Ghosh, Sen, Jha, & Pal, 2010; Pal, Nasim, Patra, Ghosh, & Panda, 2010), their uses as flocculants are limited due to their low solubility and dramatic viscosity development in some cases. To modulate and improve the characteristics and flocculation activities of carbohydrate-based polymers, thus, they are chemically modified with anionic or cationic reacting reagents. For purposes of industrial uses (as carbohydrate-based flocculants), cationic moieties such as 2,3-epoxypropyltrimethylammonium chloride (ETMAC) and 3-chloro-2-hydroxypropyltrimethylammonium chloride (CHPTAC) are often synthesized with carbohydrate-based polymers (Pal, Mal, & Singh, 2006). To date, some studies to graft the cationic moieties onto carbohydrate-based polymers have been conducted for starch amylopectin (Larsson & Wall, 1998), granular starch (Auzély-Velty & Rinaudo, 2003), guar gum (Banerjee et al., 2013), dextran (Nichifor, Stanciu, & Simionescu, 2010) and glycogen (Pal et al., 2006). These cationic carbohydrate-based polymers were traditionally prepared in aqueous or aqueous–alcoholic reaction media containing relatively high concentration of alkali. This reaction system commonly requires relatively long reaction time and did not be applied to high concentration of carbohydrate-based polymers in which their viscosity is developed to the greater extents.

To resolve the noted limitations of a conventional cationization reaction, ultra high pressure (UHP)-assisted reaction is considered

as its alternative way. UHP-assisted reaction was recently designed for starch chemical modification and applied to preparation of acid-thined starch, hydroxypropylated starch, acetylated starch, phosphorylated starch, and phosphorylated cross-linked starch (Kim, Kim, & Baik, 2012). Tanaka (1968) suggested the effects of ultra high pressure on inorganic chemical reactions as following: (1) the reaction equilibrium constant may be shifted by pressurization when an overall volume of the reaction system is changed, (2) the reaction may be accelerated by pressurization, and (3) the new reaction pathway may be generated by pressurization, radically altering the reaction products. These suggestions were somewhat fitted to UHP-assisted starch chemical modification. In UHP-assisted acetylation and hydroxypropylation reactions, reaction times was reduced to the greatest extents, although starch reactivities were around 25% lower relative to conventional reaction (Choi, Kim, Park, Kim, & Baik, 2009; Kim, Choi, Kim, & Baik, 2010, 2011; Kim et al., 2012). Kim et al. (2012) reported production of phosphorylated starch in UHP-assisted cross-linking reaction with sodium trimetaphosphate (STMP), though cross-linked starch was intended. Consequently, application of UHP in cationization reaction anticipates the reduced reaction time and characteristic of cationic carbohydrate-based polymers different from those prepared by conventional reaction.

Cationization of carbohydrate-based polymers with ETMAC and CHPTAC enhanced their solubility in cold and/or hot water and viscosity (Auzély-Velty & Rinaudo, 2003; Banerjee et al., 2013; Larsson & Wall, 1998; Pal et al., 2006). The increased viscosity of cationic carbohydrate-based polymers as flocculants is not always appropriate to wastewater treatment, because increased viscosity of wastewater by flocculant addition may make separation between floc and liquid difficult. One of the carbohydrate-based polymers, dextrin, produced through hydrolysis of starch with acids and enzymes, possesses the branched molecular structure with lower molecular weights (relative to starch amylopectin) (Lotfy, 2009; Pal et al., 2010; Ramos et al., 2006; Sharma et al., 2010). The structural characteristics of dextrin resulted in higher solubility and lower viscosity even at somewhat higher concentrations (Brossard, Du, & Miller, 2008). Thus, it is thought that dextrin is one of the best carbohydrate-based polymer sources to prepare the biodegradable flocculants by cationization reaction with ETMAC and CHPTAC.

The objectives of this study were to prepare cationic dextrins using conventional and UHP-assisted cationization reactions and to investigate and compare characteristics of traditional and UHP-assisted cationic dextrins so as to assess availability of cationic dextrins as flocculants and validate application of UHP-assisted reaction as an alternative way of traditional reaction.

2. Materials and methods

2.1. Materials

Dextrin (dextrose equivalent [DE] 12; 7.89% moisture content) was purchased from Roquette Corporation (Gurnee, IL, USA). Quaternary ammonium compound, 2,3-epoxypropyltrimethylammonium chloride (ETMAC) (73%, liquid form), was obtained from KCI Co. (Seosan, Chungnam, Republic of Korea). Analytical grades of sodium hydroxide (NaOH) and isopropanol were obtained from Daejung Chemicals & Metals Co. (Siheung, Gyeonggi, Republic of Korea).

2.2. Preparation of cationic dextrins

Compositions of the reaction mixtures for conventional and UHP-assisted cationization reaction were depicted in Table 1. The cationization reaction was conducted with A and B reaction mixtures containing low (Wang et al., 2009) and high (Kavaliauskaite, Klimaviciute, & Zemaitaitis, 2008) addition levels of ETMAC, respectively. The molar ratios of AGU (anhydrous glucose unit) to ETMAC were 1:1.5 for A reaction mixture and 1:1.77 for B reaction mixture. In sample identification in the first column of Table 1, the capital letters of A and B indicated the types of reaction mixtures, and the numbers next to the capital letters meant the applied pressure levels (MPa). For conventional cationization reaction as a reaction control, dextrin was dissolved in double-distilled water (DDW) in a three-neck flat-bottom flask at 25 °C. Subsequently, ETMAC and NaOH were added to the flask and the flask was sealed with rubber septa. The reaction was conducted at 25 °C for 5 h under continued stirring. For UHP-assisted cationization reaction, the reaction mixture was prepared in a retort pouch as listed in Table 1, and sealed using a heat sealer. The reaction mixture was pressurized at 100, 300 and 500 MPa for 30 min in high hydrostatic pressure equipment (CIP-S, Ilshin Autoclave. Co., Daejeon, Republic of Korea). During pressurization, a pressurizing chamber and retort pouch containing the reaction mixture were maintained at 25 °C. After completion of both conventional and UHP-assisted reaction, the reaction mixtures were neutralized with 1 M HCl, and mixed with 6 volumes of isopropanol to precipitate cationic dextrins. The precipitates were recovered by centrifugation ($3000 \times g$, 30 min), washed three times with excess isopropanol to remove side-reaction products and unreacted ETMAC, and dried at 105 °C for 24 h. Dried cationic

Table 1
Reaction parameters for UHP-assisted cationization of dextrins, and mean[A] values for nitrogen content and degree of substitution (DS) of native and cationic dextrins.

Samples	Reaction conditions						Nitrogen content (%)	DS
	Dextrin (g)	ETMAC[B] (g)	NaOH (g)	DDW[C] (ml)	Pressure (MPa)	Time (min)		
Native	–	–	–	–	–	–	0.08 ± 0.01	–
A0[D]	30	60	1.50	150	0.1	300	4.05 ± 0.19^e	0.81 ± 0.07^e
A100[D]	30	60	1.50	150	100	30	3.23 ± 0.10^h	0.58 ± 0.03^h
A300[D]	30	60	1.50	150	300	30	3.50 ± 0.15^g	0.65 ± 0.04^g
A500[D]	30	60	1.50	150	500	30	3.92 ± 0.10^f	0.76 ± 0.03^f
B0[D]	30	71	0.53	37	0.1	300	4.93 ± 0.08^c	1.18 ± 0.04^c
B100[D]	30	71	0.53	37	100	30	5.15 ± 0.10^b	1.30 ± 0.06^b
B300[D]	30	71	0.53	37	300	30	5.48 ± 0.13^a	1.51 ± 0.09^a
B500[D]	30	71	0.53	37	500	30	4.38 ± 0.11^d	0.93 ± 0.05^d

[A] Mean values of three replicate measurements; values sharing the lowercase letters within columns are not significantly different ($p < 0.05$).
[B] 2,3-Epoxypropyltrimethylammonium chloride.
[C] Double distilled water.
[D] The capital letters of A and B mean cationic dextrins prepared under reaction conditions at the low and high addition levels of ETMAC, respectively, and the numbers next to the capital letters indicates pressure levels applied for UHP-assisted cationization of dextrins.

dextrins were ground and stored in a dessicator at 25 °C for further analysis.

2.3. Degree of substitution (DS)

Nitrogen content (%) of dextrin samples was determined by a semi-micro Kjeldahl method. Degree of substitution (DS) was calculated as following:

$$DS = \frac{162 \times N\%}{14 \times 100 - 151.5 \times N\%}$$

where N% is nitrogen content (%) determined by a semi-micro Kjeldahl method, 162 is the molecular weight of anhydrous glucose unit, 151.5 is the molecular weight of ETMAC, and 14 represents for the nitrogen atomic mass.

2.4. FT-IR spectroscopy

FT-IR analysis of ETMAC, and native and cationic dextrins was conducted in a solid state using Spectrum One System (PerkinElmer, Waltham, MA, USA). The samples were mixed with potassium bromide (KBr) (1:100, w/w) and compressed to form a clear disk. The spectra were obtained with a resolution of 4 cm^{-1} and a wavelength range of 500–4000 cm^{-1}.

2.5. ^{13}C NMR spectroscopy

The ^{13}C NMR spectra of native and cationic dextrins were obtained using a 300 MHz nuclear magnetic resonance spectrometer (JNM-AL300, JEOL, Tokyo, Japan). The Samples were dissolved in D$_2$O at 80 °C and the analysis was carried out at a chemical shift range of 40–100 ppm (25 °C).

2.6. Thermogravimetric analysis (TGA)

The thermogravimetric (TG) and derivative thermogravimetric (DTG) analyses of the samples were carried out with thermogravimetric analysis (TGA) instrument (Q5000 IR, TA Instruments, New Castle, DE, USA). The measurement was performed at a temperature range of 25–600 °C with a heating rate of 10 °C/min in an inert atmosphere of nitrogen.

2.7. Intrinsic viscosity

Intrinsic viscosity of native and cationic dextrins was measured according to a method of Nayak and Singh (2001) with slight modification. Measurements were carried out with a capillary viscometer at 25 °C. The time when dextrin solutions (0.02–0.10 g/ml) pass through a certain section of viscometer was recorded. Intrinsic viscosity ($\mu_{intrinsic}$) was calculated as following:

$$\mu_{rel} = \frac{\rho \times t}{\rho_0 \times t_0} \tag{2}$$

$$\mu_{sp} = \mu_{rel} - 1 \tag{3}$$

$$\mu_{red} = \frac{\mu_{sp}}{C} \tag{4}$$

$$\mu_{intrinsic} = \lim_{c \to 0} \mu_{red} \tag{5}$$

where t and t_0 were the times when dextrin solution and DDW passed through a certain section of viscometer, respectively, ρ and ρ_0 were the densities of dextrin solution and DDW at 25 °C, respectively and C was the concentration of dextrin solutions (g/ml). μ_{rel}, μ_{sp} and μ_{red} referred to relative, specific and reduced viscosity, respectively.

2.8. Flocculation test

Flocculation test of native cationic dextrins were carried out according to a method of Shogren (2009). Kaolin (1 g) was mixed with DDW (100 g) in a 150-ml beaker under continuous stirring (2.5 cm [in length] magnetic bar, 450 rpm, 5 min). Stirring speed was reduced to 300 rpm, and the required amounts of native and cationic dextrins (final concentrations was 10, 40, 70, and 100 ppm) were added. The mixtures were stirred for additional 2 min, after which stirring speed was further reduced to 180 rpm (just enough to keep kaolin in suspension) for 5 min. Then, the floc was allowed to settle down for 2 min without stirring. After the settling period, aliquots were taken at half height of the liquid column for measurement of percent transmittance at 670 nm using UV-1200 Spectrophotometer (Labentech, Incheon, Republic of Korea).

For effect of settling time on flocculation of kaolin, 40 ppm of native and cationic dextrins were added to kaolin solution (1 g/100 g DDW) and leave them for 10 min. During settling, aliquots were taken in every minute at half height of the liquid column for measurement of percent transmittance at 670 nm using UV-1200 Spectrophotometer (Labentech, Incheon, Republic of Korea).

2.9. Statistical analysis

The conventional and UHP-assisted cationization reactions were replicated twice for each treatment. DS values and all measurements were determined at least twice for each experimental replicate. Also, experimental data were analyzed using Analysis of Variance (ANOVA), and expressed as mean value ± standard deviation. Significant differences among experimental mean values were assessed by a Duncan's multiple range test ($\alpha < 0.05$). All statistical computations and analyses were conducted using SAS version 9.02 for Windows (SAS Institute, Inc., Cary, NC, USA).

3. Results and discussion

3.1. Nitrogen content and degree of substitution (DS)

Nitrogen content (%) and degree of substitution (DS) of native and cationic dextrins were listed in Table 1. A nitrogen content of native dextrin was 0.08%, while those of cationic dextrins were in a range of 3.23–5.48%. The enhanced nitrogen contents of cationic (relative to native) dextrins suggested that quaternary ammonium groups of cationizing reagent (ETMAC) were successfully substituted onto hydroxyl groups of dextrin backbones.

DS values (0.58–0.81) of A reaction group with the lower ETMAC addition level were lower than those (0.93–1.51) of B reaction group with the higher ETMAC addition level. These results were possibly due to larger amount of ETMAC in B (relative to A) reaction group. Also, excess amount of NaOH and water in A reaction group may induce the partial hydrolysis and side-reaction of ETMAC forming unexpected product (Kavaliauskaite et al., 2008). For B (relative to A) reaction group, furthermore, ETMAC appeared to be much more accessible to dextrin molecules, because B reaction group exhibited lower total volume of the reaction mixture and higher ratio of dextrin to ETMAC than A reaction group (Tanaka, 1968).

Regarding A reaction group conducted with lower ETMAC addition level and larger reaction mixture volume, cationic dextrin (A0) subjected to conventional reaction revealed the higher DS than those (A100, A300, A500) subjected to UHP-assisted reaction (Table 1). These results may be due to differences in reaction

time between conventional (300 min) and UHP-assisted (30 min) reactions, as already reported in UHP-assisted hydroxypropylation reaction of starch (Kim et al., 2011). For UHP-assisted cationization reaction, DS values of cationic dextrins increased with increasing pressure levels from 100 to 500 MPa (Table 1). The findings paralleled the results of Choi et al. (2009) and Kim et al. (2011), who reported the enhanced reactivities (determined by DS) of starch granules in UHP-assisted substitution reaction with acetic anhydride and propylene oxide, respectively, with increasing pressure levels from 200 to 400 MPa. Moreover, a maximum DS value (0.76) was observed for cationic dextrin prepared at 500 MPa, and very approximated to that (0.81) prepared by conventional reaction (Table 1). This result suggested that an increase of the pressure level appeared to promote cationization of dextrin with ETMAC, ultimately reducing reaction time. In the A reaction group, 90% reduction in reaction time was achieved, as the cationic dextrin prepared at 500 MPa was compared with that by conventional reaction. On the other hand, in B reaction group conducted with higher ETMAC addition level and smaller reaction mixture volume, DS values (1.30–1.51) of UHP-assisted cationic dextrins (B100, B300), except for that prepared at 500 MPa (B500), were over that (1.18) of conventional cationic dextrin (B0) (Table 1). The increase of pressure levels from 100 to 300 MPa enhanced reactivities of dextrin molecules, and the maximum DS value was observed for cationic dextrin prepared at 300 MPa. However, the pressure level of 500 MPa decreased the DS value (0.93) of UHP-assisted (relative to conventional) cationic dextrin. This finding may be explained by the presence of heavily-reacted dextrin molecules which may possess much more hydroxypropyl and methyl groups, and cations, thus enhancing their solubilities in aqueous isopropanol and/or isopropanol. Consequently, heavily-reacted dextrin molecules may be lost during post-treatments (precipitation and washing with isopropanol) after completion of reaction, lowering the DS value (determined as average values) of cationic dextrin. Moreover, application of UHP in B (relative to A) reaction group could reduce the reaction time when UHP-assisted cationic dextrins achieved DS levels similar to those of conventional cationic dextrins to the greatest extents. Overall, the apparent total volume of the reaction mixtures was compressed by UHP, which may enhance the probability of alkoxide ions of dextrin molecules in an alkaline solution contacting ETMAC. Thus, reaction of dextrin molecules with ETMAC may be facilitated and accelerated, resulting in the increased DS values of UHP-assisted cationic dextrins. Furthermore, based on DS value and reaction time, the reaction system applied to B reaction group (Table 1) was more appropriate for UHP-assisted cationization reaction of dextrins.

3.2. FT-IR spectroscopy

FT-IR spectra of ETMAC, and native and cationic dextrins were shown in Fig. 1. Native dextrin possessed the broad bands at 3390 and 2930 cm^{-1} resulting from the stretching vibration of O—H and C—H bonds, respectively. Also, the bands at 1156, 1081 and 1019 cm^{-1} which are attributed to the stretching vibration of C—O bond in the anhydrous glucose unit (AGU) were revealed. In a case of ETMAC, the bands at 3398, 3023 and 1480 cm^{-1} were observed for the O—H, C—H and C—N bonds, respectively (Lin et al., 2012). Further, a strong band was present at 1265 cm^{-1}, corresponding to epoxy ether (Wang & Xie, 2010). On the other hand, all cationic dextrins prepared by both conventional and UHP-assisted reactions exhibited the bands observed in the spectrum of native dextrin as well as an additional band at 1490 cm^{-1} assigned to the stretching vibration of C—N bond. These observations provided obvious evidence that cationic moiety of ETMAC was successfully incorporated onto the dextrin backbone, as reported by Wang et al. (2009).
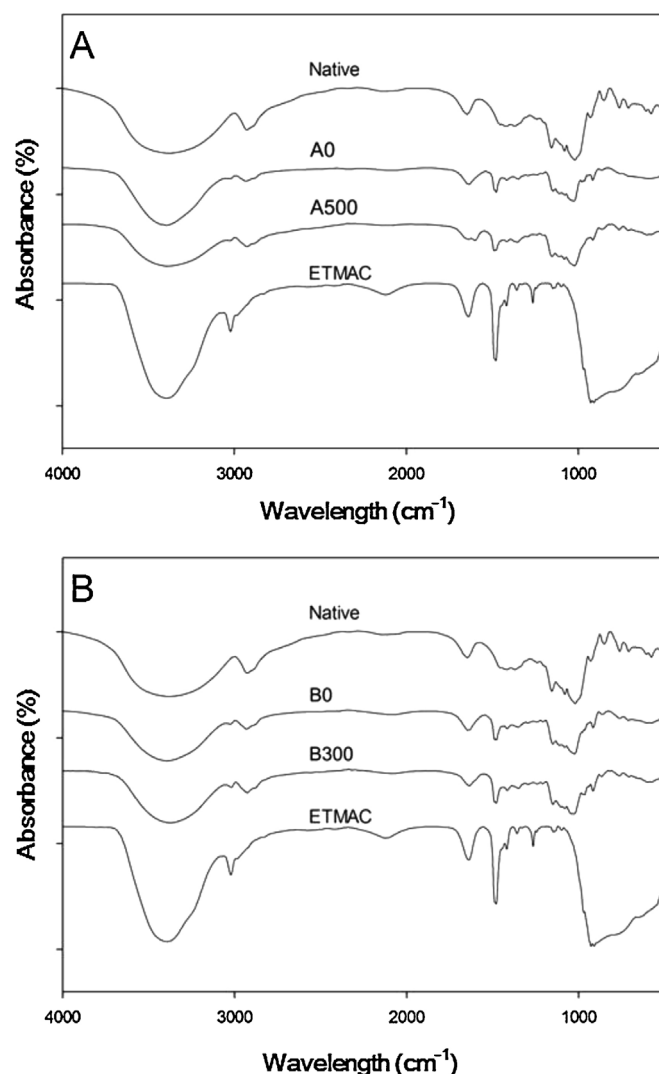

Fig. 1. Fourier transform-infrared spectroscopy (FT-IR) spectra of ETMAC, native dextrin, and cationic dextrins prepared under reaction conditions at the low (A) and high (B) addition levels of ETMAC. In the legends, the numbers next to the capital letters (A and B) indicates pressure levels (MPa) applied for UHP-assisted dextrin cationization.

3.3. ^{13}C NMR spectroscopy

To further confirm successful reaction of dextrin with ETMAC, native and cationic dextrins were examined with ^{13}C NMR, and their spectra were depicted in Fig. 2. Native dextrin exhibited six intense peaks in the chemical shift ranges of 60–100 ppm, indicating carbons of the unreacted AGU. The six peaks observed at 99.9, 71.8, 73.5, 77.0, 71.4, and 60.7 ppm were attributed to the C-1, C-2, C-3, C-4, C-5 and C-6 within AGU, respectively. Both spectra of conventional and UHP-assisted cationic dextrins revealed additional peaks at 68.5, 66.8 and 55.5 ppm which resulted from the C-9, C-8 and C-10 in the cationic moieties, respectively (Haack, Heinze, Oelmeyer, & Kulicke, 2002). Moreover, original peaks of native dextrin were divided and/or shifted downward. Overall observations provided strong evidence that the cationic groups of ETMAC were successfully substituted on dextrin backbones.

3.4. Thermogravimetric analysis (TGA)

The thermal properties of native and selected cationic dextrins were examined by thermogravimetric (TG) and derivative
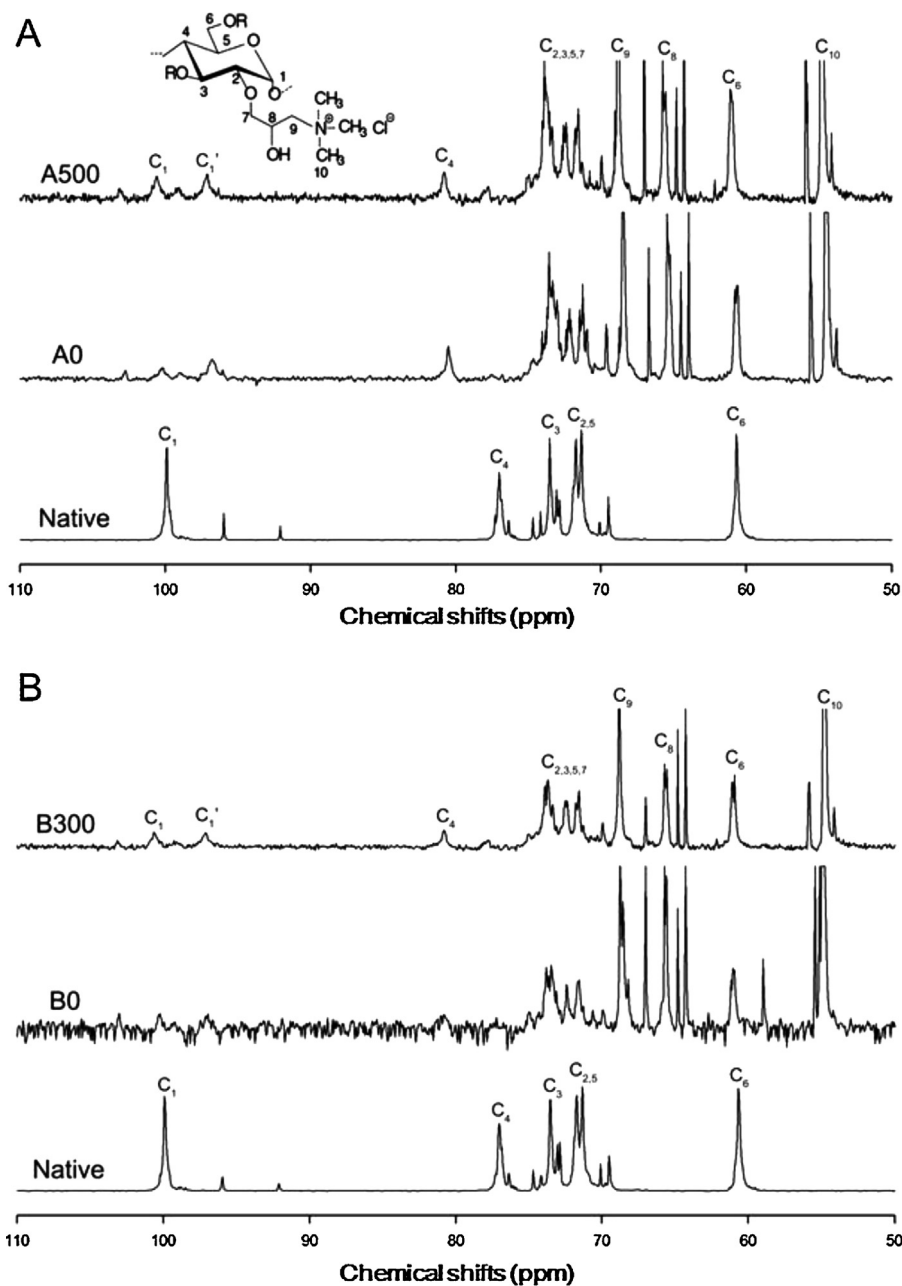
Fig. 2. ^{13}C nuclear magnetic resonance (NMR) spectra of native dextrin and cationic dextrins prepared under reaction conditions at the low (A) and high (B) addition levels of ETMAC. In the legends, the numbers next to the capital letters (A and B) indicates pressure levels (MPa) applied for UHP-assisted dextrin cationization.

thermogravimetric (DTG) analyses, and depicted in Fig. 3. TGA curves show the temperature range that samples were lose their weight, and the peaks of DTG curves offer the decomposed temperature of samples (Wang & Xie, 2010). The initial weight losses of dextrin samples observed at the temperature range of 30–120 °C were due to evaporation of trace moisture in the dextrin samples. Their second weight losses were observed near at 300 °C, indicating the decomposition of dextrin samples. While native dextrin was decomposed at 310.31 °C, all cationic dextrins subjected to conventional and UHP-assisted reactions under different A and B reaction systems were decomposed at the temperature ranges of 262.55–281.55 °C (Fig. 3). These results were compatible with the observation of Wang and Xie (2010), who reported that thermal stability of cationic dextins was reduced. Consequently, it was

obvious that the cationized dextrins were degraded at relatively lower temperature than its native forms.

With respect to cationic dextrin, in A reaction group, the thermal decomposition temperature (281.55 °C) of UHP-assisted cationic dextrin (A500) was higher than that (270.35 °C) of conventional counterpart (A0) (Fig. 3A), though similar DS values were observed for conventional (0.81) and UHP-assisted (0.76) cationic dextrins (Table 1). These findings may be due to differences in degree of alkaline degradation of dextrin molecules during when dextrin molecules reacted with ETMAC in an alkali solution. Heinze, Haake, and Rensing (2004) reported lower molecular weights of cationic starches (wheat, potato, and waxy, normal, and high-amylose corn) than those of their respective native starches, resulting from degradation of starch molecules (amylopectin and amylose) by
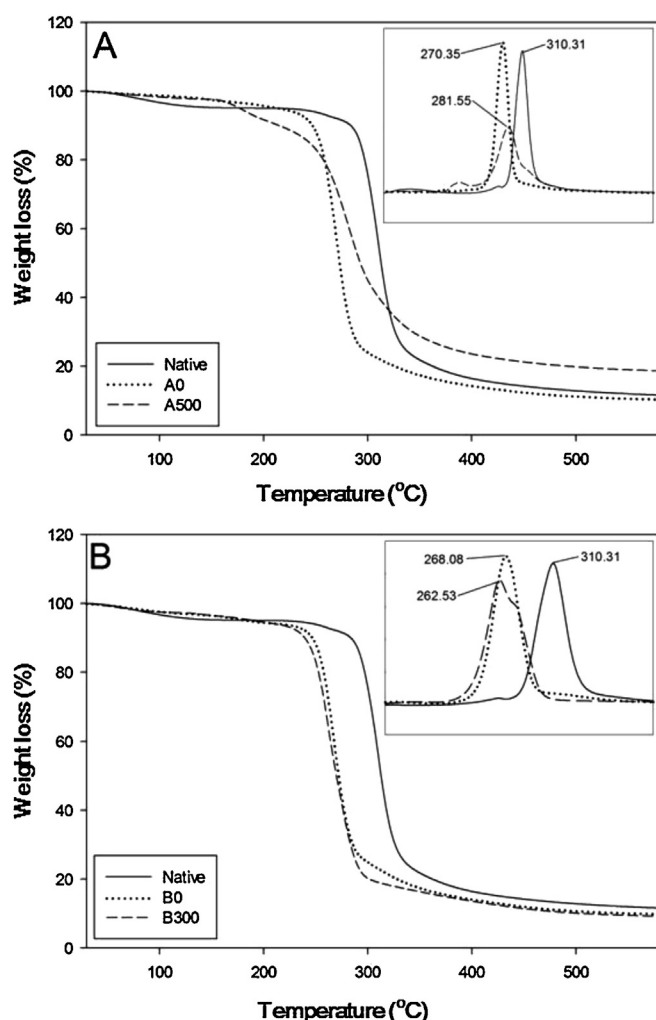
Fig. 3. Thermogravimetric (TG) and derivative thermogravimetric (DTG) curves of native dextrin and cationic dextrins prepared under reaction conditions at the low (A) and high (B) addition levels of ETMAC. In the legends, the numbers next to the capital letters (A and B) indicates pressure levels (MPa) applied for UHP-assisted dextrin cationization.

Fig. 4. Intrinsic viscosities of native and cationic dextrins. In the sample names of X-axis, the capital letters of A and B mean cationic dextrins prepared under reaction conditions at the low and high addition levels of ETMAC, and the numbers next to the capital letters (A and B) indicates pressure levels (MPa) applied for UHP-assisted dextrin cationization.

3.5. Intrinsic viscosity

Intrinsic viscosities ($\mu_{intrinsic}$) of native and cationic dextrins were determined using a capillary viscometer, and shown in Fig. 4. In general, the $\mu_{intrinsic}$ of protein- and carbohydrate-based hydrocolloids were well-known as an indirect criterion to assess their molecular weights (Cho, Kim, & Rhim, 2003). The $\mu_{intrinsic}$ of all cationic dextrins investigated were in the ranges of 7.520–14.87 l/g, although native dextrin was 4.04 l/g (Fig. 4). The phenomenon that cationic (relative to native) dextrins exhibited higher $\mu_{intrinsic}$ (though degradation of dextrin by cationization was inferred from TG–DTG analysis results) may be due to both their enhanced molecular weight and further extended structural conformation. Cationic dextrins (containing their degraded fragments) possessed considerable bulky substituents (ETMAC), increasing their molecular weights. Moreover, structural conformation of cationic (relative to native) dextrin molecules may be more extended due to bulky substituents incorporated onto native dextrin molecules which may exhibit the mixed forms of compact and random-coil conformation (BeMiller, 2007). Noted changes in structural characteristics of native dextrin molecules by cationization resulted in increase of its hydrodynamic volume, enhancing $\mu_{intrinsic}$ (determined using the capillary viscometer) of cationic dextrin. Within cationic dextrins, on the other hand, $\mu_{intrinsic}$ was higher for conventional (relative to UHP-assisted) reaction in A reaction group, while the opposite pattern was present in B reaction group. These inconsistent trends were coincided with those observed for thermal stability (determined by TG–DTG analyses) of cationic dextrins (Fig. 3). Thus, the findings observed from $\mu_{intrinsic}$ appeared to further support that differences in thermal stability between conventional and UHP-assisted cationic dextrins may be influenced by alkaline degradation of dextrin molecules during cationization, as suggested from TG–DTG analyses of cationic dextrins.

3.6. Flocculation test

Cationic dextrin molecules ionically bind with negatively-charged particles in wastewater, forming bridges among negatively-charged particles. Interconnection of negatively-charged particles by cationic dextrin molecules generates huge flocs that are settled down (Gregory & Barany, 2011). In this study, thus, the modified jar test was accepted to evaluate flocculating

cationization reaction. Han and Lim (2004) revealed more degradation of amylopectin (relative to amylose) molecules with increasing a dissolution time when corn starch was held in NaOH solution (1 M). Consequently, the findings observed in A reaction group suggested less thermal stability of conventional cationic dextrin, due to the fact that during conventional (relative to UHP-assisted) cationization, dextrin was much longer exposed to the alkaline reaction solution, further facilitating its degradation to more extents.

In the case of cationic dextrins in B reaction group, the decomposition temperature (268.08 °C) of conventional cationic dextrin was higher than that (262.53 °C) of UHP-assisted cationic dextrin (Fig. 3B), which was opposite to the result observed in A reaction group (Fig. 3A). This phenomenon was explained by the enhanced accessibility between dextrin molecules and cationizing reagent/catalyst by UHP treatment, as supported by higher DS values of UHP-assisted (relative to conventional) cationic dextrins (Table 1). Under UHP, dextrin molecules more frequently contacted with NaOH (catalyst in cationization reaction) as well as ETMAC, facilitating dextrin molecular degradation and reaction of dextrin molecules with ETMAC together. Different from findings in A reaction group, thus, poor thermal stability was observed for UHP-assisted (relative to conventional) cationic dextrins.
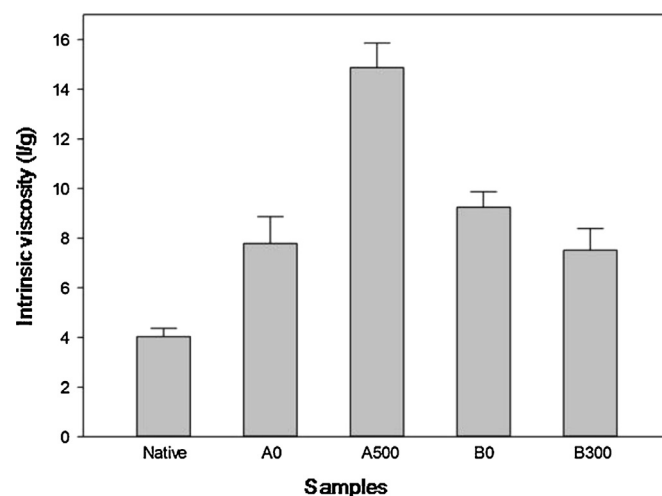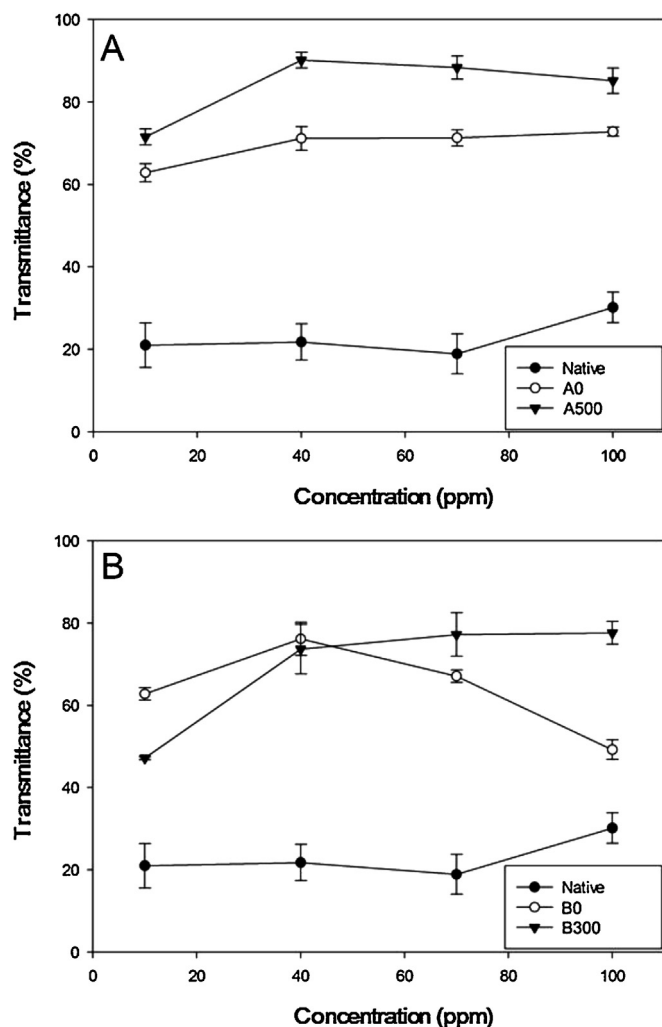
Fig. 5. Effects of concentrations of native and cationic dextrins on flocculation of kaolin in water. In the legends, the capital letters of A and B mean cationic dextrins prepared under reaction conditions at the low and high addition levels of ETMAC, and the numbers next to the capital letters (A and B) indicates pressure levels (MPa) applied for UHP-assisted dextrin cationization.

Fig. 6. Influences of settling time on flocculation of kaolin in water (measured by light transmittance at starch concentration of 40 ppm). In the legends, the capital letters of A and B mean cationic dextrins prepared under reaction conditions at the low and high addition levels of ETMAC, and the numbers next to the capital letters (A and B) indicates pressure levels (MPa) applied for UHP-assisted dextrin cationization.

activity of cationic dextrins (Figs. 5 and 6). To investigate the optimum doses of cationic dextrins as flocculants, native and cationic dextrins were tested in the ranges of 10–100 ppm (Fig. 5). Native dextrin showed low flocculating activities, regardless of tested concentrations. In contrast, cationic (relative to native) dextrins revealed much higher flocculating activities over all tested concentration. In the case of A reaction group with lower ETMAC addition level, flocculating activities of UHP-assisted cationic dextrins were higher than those of conventional counterparts (Fig. 5A). For B reaction group with higher ETMAC addition levels (Fig. 5B), similar patterns were observed, except for 10 ppm of cationic dextrin in which conventional cationic dextrin possessed higher flocculating activities than UHP-assisted cationic dextrin. These results indicated that cationic dextrins prepared through UHP-assisted (relative to conventional) reaction provided much higher flocculating activities.

On the other hand, the effects of settling time on flocculating activities of cationic dextrins were investigated, and described in Fig. 6. Although native dextrin did not possess flocculating activity, all cationic dextrins tested in this study showed rapid flocculation, and achieved the maximum flocculation at the settling time of 2–4 min. Cationic dextrins can be easily adsorbed to the colloid surface of anionic kaolin suspensions due to their electrostatic
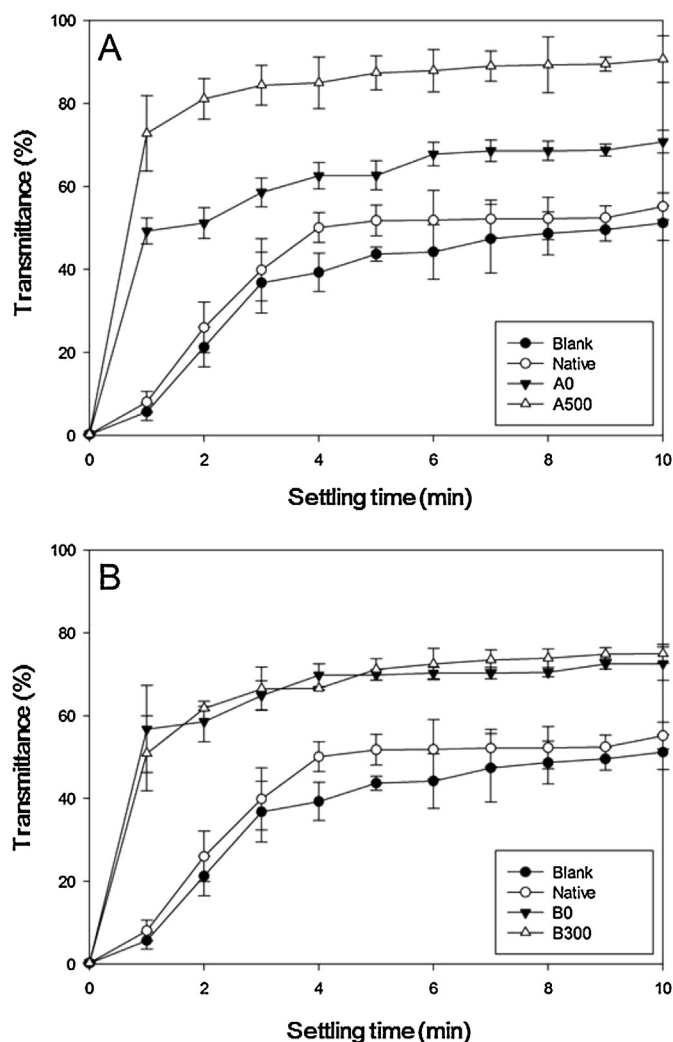
attraction, resulting in rapid flocculation (Wei et al., 2008). UHP-assisted cationic dextrin in A reaction group revealed higher flocculating activity than conventional cationic dextrin (Fig. 6A), though similar DS values were obtained for both cationic dextrins (Table 1). For B reaction group, however, any significant differences in flocculating activity were not observed for conventional and UHP-assisted cationic dextrins (Fig. 6B), even though DS value of UHP-assisted cationic dextrin was greater than that of conventional cationic dextrin (Table 1). Further, comparing conventional dextrins in A reaction group to in B reaction group, flocculating activities were similar, although DS values were different for both reaction groups. These findings suggested that flocculating activities were not likely influenced by DS values of cationic dextrin and cationization reaction methods. Nevertheless, maximum flocculating activity was achieved for UHP-assisted cationic dextrins in A reaction group (Fig. 6A). Recalling results of $\mu_{intrinsic}$ of cationic dextrins, UHP-assisted cationic dextrin in A reaction group exhibited the highest $\mu_{intrinsic}$ than conventional cationic dextrin in A reaction group and cationic dextrins in B reaction group. However, $\mu_{intrinsic}$ was similar for conventional cationic dextrin in A reaction group and cationic dextrins in B reaction group, which revealed

similar flocculating activities. Pal et al. (2006) suggested that polymers with higher viscosity possessed better flocculating activities. Overall findings suggested that viscosity (influenced by molecular weight and structural conformation) of cationic dextrins may be a crucible factor of determining their flocculating activity.

4. Conclusions

This study applied UHP-assisted derivatization method to reaction of dextrin with ETMAC, and investigated flocculating activity of cationic dextrins. UHP-assisted cationization reaction successfully substituted hydroxyl groups of dextrin molecules with ETMAC, as supported by FT-IR and ^{13}C NMR analyses. UHP-assisted cationization exhibited the general trends in increasing reactivity (determined by DS values) of dextrin with increasing applied pressure levels, although some variations were present depending on reaction systems. Further, this study confirmed that DS values of UHP-assisted cationic dextrins could exceed those of conventional cationic dextrins in the reaction system with relatively higher ETMAC levels and smaller volume of the reaction mixtures (B group). Thus, if UHP-assisted reaction would be considered for chemical modification of carbohydrate-based hydrocolloids, the reaction parameters such as the molar ratio of carbohydrate substrates to reacting reagents, catalyst concentration, final volume of reaction mixtures, pressure, and pressurizing time would be crucible factors to construct UHP-assisted chemical modification reaction. Also, UHP-assisted cationization reaction likely required shorter reaction time to achieve similar DS values to those of conventional cationic dextrins. Consequently, UHP-assisted cationization reaction can be an alternative way of preparing cationic dextrins via conventional reaction, and an efficient and energy-saving method to reduce the reaction time (from 300 to 30 min). On the other hand, cationic dextrins prepared by conventional and UHP-assisted reactions exhibited remarkable improvement in the flocculation test using kaolin suspension. Thus, it is clear that the cationic dextrin is a promising material to replace the synthetic flocculant as an environment-friend flocculant for the wastewater treatment.

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